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# The effect of a 3-methacryloxypropyltrimethoxysilane and vinyltriisopropoxysilane blend and *tris*(3-trimethoxysilylpropyl)isocyanurate on the shear bond strength of composite resin to titanium metal

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## KEYWORDS

Silane; Fourier transformation infrared spectroscopy; Dental materials; Titanium; Adhesion

**Summary Objectives.** The aim of this study was to evaluate the reactions of silanes prior to attaching the composite to titanium and evaluate these silanes as coupling agents. Veneered titanium may be used as a prosthetic material.

**Methods.** Two silane solutions, a mixture of both  $\gamma$ -methacryloxypropyltrimethoxysilane and vinyltriisopropoxysilane, and *tris*(3-trimethoxysilylpropyl)isocyanurate were prepared as 2 wt% in two different (95% 2-propanol and 90% acetone) solutions. A control, 2 wt%  $\gamma$ -methacryloxypropyltrimethoxysilane was prepared in both solutions. These six silane solutions were applied onto flat titanium surfaces. The samples ( $N = 250$ ) were divided into two main groups: air-dried (room temperature) and heat cured for 1 h at 110 °C. Sinfony<sup>®</sup> veneering composite was applied and light-cured on the titanium. The control group was non-silanized. The specimens were assigned to two subgroups: not thermocycled, and thermocycled (5000 cycles, 5–55 °C). Shear bond strength of the composite was tested at a crosshead speed of 1.0 mm min<sup>-1</sup>. Fresh silane solution hydrolysis, and condensation reaction on titanium surface were monitored by FTIR spectrometry.

**Results.** Dry samples could be successfully tested, while thermocycling after 3700 cycles had gradually de-bonded the composite from the silanized titanium substrate. For dry samples, statistical analysis (ANOVA) showed that solvent and silane significantly affected the shear bond strength. The silane mixture in 2-propanol reacted at room temperature yielded 11.3 MPa (Standard deviation, SD, 3.6 MPa) and on the other hand, *tris*(3-trimethoxysilylpropyl)isocyanurate in 2-propanol yielded 10.7 MPa (SD 8.0 MPa) and  $\gamma$ -methacryloxypropyltrimethoxysilane 20.4 MPa (SD 12.2 MPa). Non-silanized samples yielded 4.8 MPa (SD 2.1 MPa).

**Significance.** In all solvents used, silanes reacted chemically with the titanium surface and covalent Si-O-Ti- and -Si-O-Si- bonds were evident.

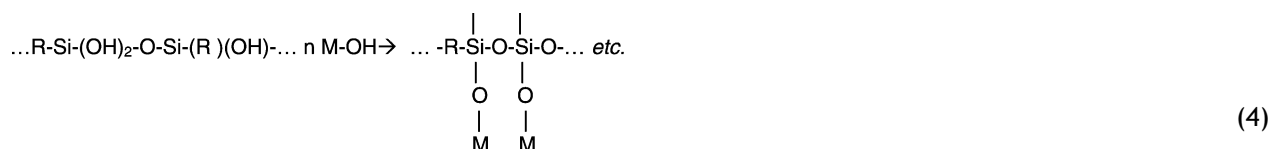
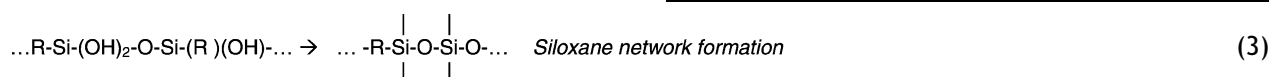
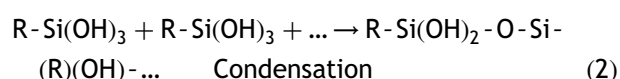
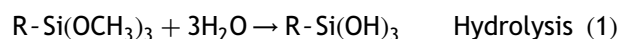
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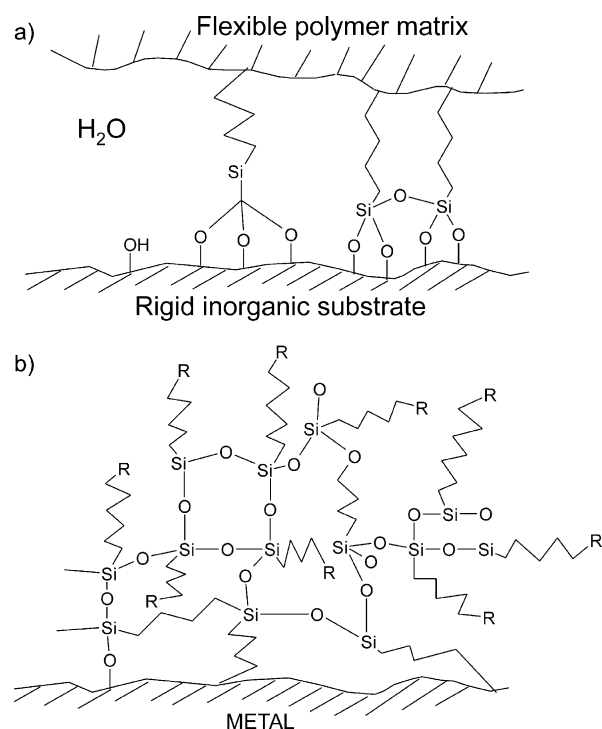
## Introduction

The use of especially bifunctional trialkoxysilane coupling agents to join different materials was previously based on vinyltriethoxysilane and *tris*(2-methoxyethoxy)vinylsilane<sup>1</sup> and first used in plastics industry applications.<sup>2</sup> Later development work introduced  $\gamma$ -methacryloxypropyltrimethoxysilane (MPS, or MPTS),<sup>3</sup> which became superior to vinylsilane for dental applications.<sup>4</sup> Organosilanes alter the surface energy of an inorganic substrate. Organotrialkoxysilanes (hereafter: silanes), monomers, can have an organic functional radical that can co-polymerize with the composite resin. The other functional groups can be for example three methoxy ( $-\text{O}-\text{CH}_3$ ), ethoxy ( $-\text{O}-\text{CH}_2\text{CH}_3$ ), or isopropoxy ( $-\text{O}-\text{CH}(\text{CH}_3)_2$ ) groups. The alkoxy groups react acid catalyzed (or base catalyzed), in aqueous alcohol solution (see simplified descriptive reactions 1-4 below). At the first stage a hydrolysis reaction takes place: the resulting, intermediate silanol groups ( $-\text{Si}-\text{OH}$ ) can condense to form dimeric and oligomeric molecules. In the next step they rapidly form with each other stable, crosslinked siloxane bonds,  $-\text{Si}-\text{O}-\text{Si}-$  (a network, layer). With an inorganic substrate (like basic hydroxyl groups containing metals  $\text{M}-\text{OH}$ )  $-\text{Si}-\text{O}-\text{M}-$  bonds will also be formed. The two latter reactions (3) and (4) can take place simultaneously (Fig. 1(a) and (b)).<sup>5-7</sup> Hydrogen bonding between the silane molecules can also occur, (omitted from the following reactions and figures, for clarity):



### Reactions with M-OH surface

At pH 4, the rate of condensation between silanol groups of monomeric silane molecules to larger oligomers is minimized, so that the silane solutions have the highest stability. *Tris*(3-trimethoxysilylpropyl)isocyanurate is called a *tris*-functional silane, i.e. it has three silicon atoms, each of



**Figure 1** (a) Trialkoxysilane molecules acting as coupling agent, a very schematic presentation. Flexible polymer matrix corresponds to a veneering composite in the study, and a rigid inorganic matrix corresponds to used titanium metal, with hydroxyl groups on its outer surface layer. (b) Hydrolyzed trialkoxysilanes form a covalently bonded (siloxane bonds) film. Free hydrogen bonded silane molecules may also appear (not shown in the figure).

which has three hydrolysable alkoxy groups. Chemically it is also classified as an amine.<sup>8</sup> MPS and vinyltriisopropoxysilanes are monofunctional, i.e.

they both have one silicon atom with three alkoxy groups (Fig. 2). Silanes have been/are also applied as sizing chemicals for surface treatment of filler materials (e.g. silica, silicates, E-glass fibers) in dental restorative composites, in order to bond the filler matrix firmly to the composite. Vallittu has

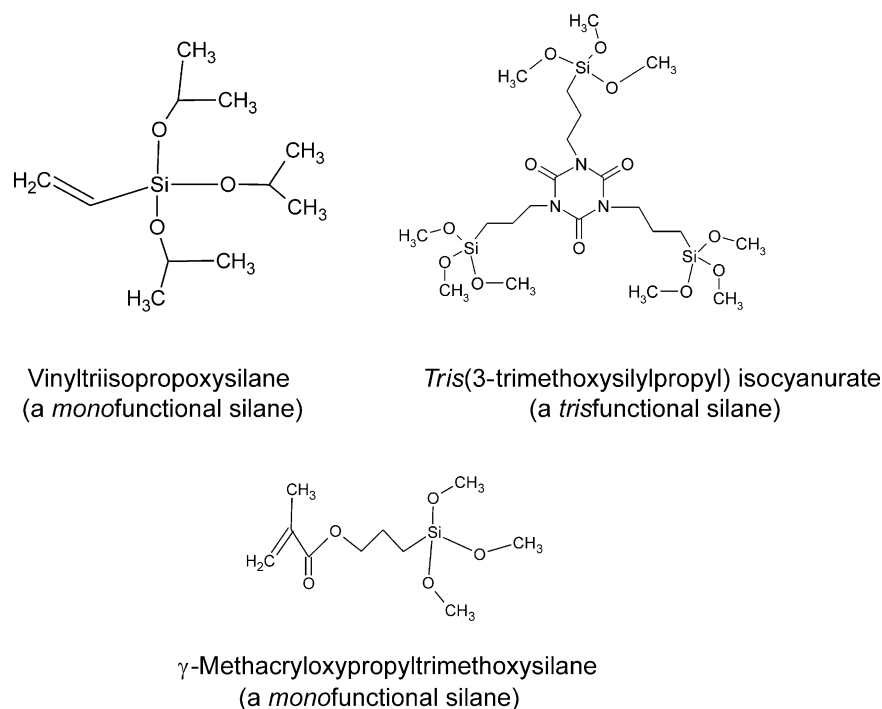


Figure 2 Molecular structures of the silanes used in this study.

applied silanes successfully onto E-glass fibers for prosthetic dental appliances in his research.<sup>9,10</sup>

Aminosilanes are applied especially with E-glass fibers and composites in non-dental applications.<sup>11</sup> In the dental context it seems that they have not shown good performance but recently a fluoride releasing system based on aminosilane has shown interesting properties.<sup>12</sup> Craig and Dootz studied some silane mixtures, in order to enhance the hydrophobic character of the filler.<sup>13</sup> MPS was reported by Craig and Mohsen to increase the hydrolytic stability of quartz and zirconium silicate fillers in composites.<sup>14</sup> Kurata and Yamazaki showed that the bond strengths and water resistance were excellent when a mixture of bisfunctional silanes and MPS was used adhering methacrylic resin to glass plates.<sup>15</sup>

Van Ooij recently studied silane mixtures and concluded that certain silane mixtures may be considerably more potent than the individual silanes alone.<sup>16</sup> Silanes have also been used as coupling agents while adhering titanium to poly (methylmethacrylate), PMMA, and to other resins,<sup>17–20</sup> or to the pre-treatment of titanium dioxide particles for a composite filler.<sup>21</sup> Silanes are incorporated in polar aqueous organic solvents, as ethanol and propanol. Methanol is unfavorable, due to its cytotoxicity. Silane coupling agents were found to improve the bonding of composite to ceramic by approximately 25%.<sup>22–24</sup> These studies

demonstrated the use of silane, or its degraded solution, to be ineffective when used on a glazed ceramic surface. Analogically, titanium metal surface roughening could be recommended. Over the past few decades, titanium has gained popularity in dentistry particularly due to its biocompatible nature. Titanium is resistant to corrosion because it instantaneously forms an extremely thin oxide layer that makes it passive. Ekstrand et al. have shown the improvement brought about by bonding veneering composite resin on the silanized titanium. In their study, a solution of 2 wt% MPS and 2 wt% *n*-propylamine was applied from cyclohexane.<sup>17</sup>

The aim of this study was to compare silane performance and adhesion of composite on titanium substrate. Non-silanized titanium substrates were used as control in the veneering tests. Cyanuratesilane and vinyltriisopropoxysilane—to the best knowledge of the authors—are not widely investigated in dentistry, were preliminarily evaluated as coupling agents between titanium and veneering composite resin. Vinyltriisopropoxysilane is a trialkoxysilane with a reactive double bond substituent, and the cyanuratesilane has three propylsilylmethoxy groups ready to hydrolyze. The latter might also form a siloxane layer with the Ti substrate. In 2-propanol, especially vinyltriisopropoxysilane, isopropoxy groups may hydrolyze more readily than e.g. in ethanol. On the other hand,

acetone-water mixture is a known medium for some prehydrolyzed silanes. The details of the solvent effects are beyond the scope of this study. Variations between the studies related to coupling agents in dental materials research led the authors to this study to compare different commonly used water-polar organic solvent mixtures for silanes. Titanium may have good potential in prosthetic dentistry.

## Materials and method

### Titanium preparation

Titanium metal used was commercially pure grade 2 (Permascand AB, Ljungaverk, Sweden, Lot ASTM B26589). Titanium was prepared and cut to ca.  $20 \times 40 \times 1 \text{ mm}^3$  planar slides ( $n = 48$ ). The surface was finished and polished with silicon carbide (SiC) paper having 1200 grits ( $0.15 \mu\text{m}$  particles). Then the slides were cleaned for 10 min in an ultrasonic bath (Quantrex 90 WT, L&R Manufacturing, Inc., Kearny, NJ, USA) and finally rinsed with ethanol and acetone, in order to remove any grease and organic impurity.

### Silane preparation

A 2.0 wt% solution i.e. 1.0 wt% of both  $\gamma$ -methacryloxypropyltrimethoxysilane (Sigma-Aldrich Chemie GmbH, Steinheim, Germany, purum 98%, Lot S01603-022) and 1.0 wt% vinyltriisopropoxysilane (Fluka Chemie, Buchs, Switzerland, purum 97%, Lot 342902/01) was prepared. Also, 1.0 wt% *tris*(3-trimethoxysilylpropyl)isocyanurate (ABCR, Karlsruhe, Germany, purum 95%, Lot 96D-1888-OD10-GSR) was prepared. The silanes were measured accurately, and rapidly moved to a 25 ml polyethylene bottle, to avoid atmospheric humidity. Then, a 95% 2-propanol (Riedel-de Haën, Seelze, Germany, pro analysi, Lot 11310), or a 90% acetone (J. T. Baker, Denventer, Holland, pro analysi, Lot 0026310001), were added, both in de-ionized water (resistivity  $18.2 \text{ M}\Omega \text{ cm}$ ). The pH was adjusted at four with 1 M acetic acid (Merck, Darmstadt, Germany, pro analysi 100%, Lot 202 K12716063), also in de-ionized water. Next the sealed silane solutions for the bonding tests were allowed to hydrolyze for 1 h at room temperature (RT,  $20^\circ\text{C}$ ).

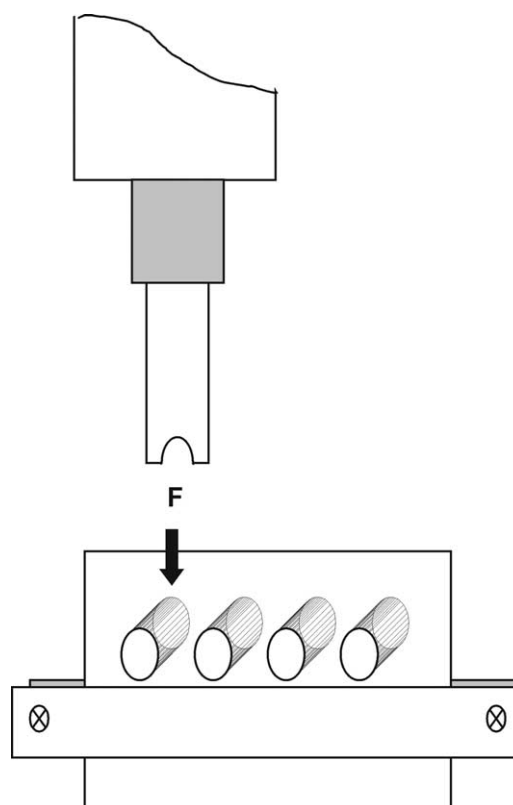
### Bonding and testing procedure

Half of the titanium slides (not the control slides) were silanized at RT, i.e. silane solution was

applied on the metal substrate surface and allowed to react for 15 min, and gently air-blasted dry. The other half ( $n = 24$ ) were silanized by brushing a thin silane layer<sup>25</sup> and heat treated for 1 h at  $110^\circ\text{C}$ . Sinfony<sup>®</sup> veneering composite (a dimethacrylate composite, ESPE GmbH, Seefeld, Germany), was applied as 2 mm diameter and 4 mm high cylindrical stubs, five on each of the horizontal borders of the Ti slides, applied in polyethylene molds and the veneering composite was placed in increments, together two layers each of which were light cured (Optilux 501, SDS Kerr, Danbury, CT, USA) for 20 s. Light-intensity was  $800 \text{ mW cm}^{-2}$ . Final polymerization was carried out in an ESPE Visio<sup>®</sup> BETA Vario (in Program 1) light-curing unit (ESPE GmbH, Seefeld, Germany), for 15 min in a vacuum. The mold was then removed carefully by pressing the cured composite to the substrate. Non-silanized Ti-substrates with the veneering resin acted as the control group.

### Shear bond tests

The shear bond test was conducted for one half of the samples in dry, room temperature conditions. The other half was subjected to thermocycling for



**Figure 3** The test set-up for bond strength measurements of silanized titanium slides with the veneering composite samples (five pieces of the composite on each titanium slide).

5000 cycles at temperatures altering between 5 and 55 °C with an immersion time of 30 s. Shear bond tests were measured with a material testing machine (LRX<sup>®</sup>, Lloyd Instrument Ltd., Farham, UK) with Nexygen<sup>®</sup> soft ware (from the same supplier), using a cross head speed of 1.0 mm min<sup>-1</sup> (Fig. 3).

## Statistical analysis

The data of this study was statistically analyzed using the two-way analysis of variance, ANOVA (SPS Inc., Chicago, IL, USA). The dependent variable (shear bond strength) was explained by the independent variables (type of silane and storage conditions).

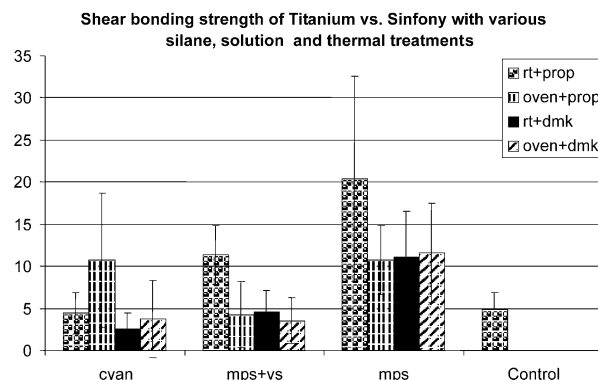
## Infrared spectroscopy

A Fourier transform infrared region (FTIR) spectrophotometer (Perkin Elmer Spectrum One, Perkin-Elmer Ltd., Beaconsfield, UK) was used at a resolution of 2 cm<sup>-1</sup> throughout the spectral range (4000–600 cm<sup>-1</sup>) by taking 32 scans (the scanning speed was 0.50 cm s<sup>-1</sup>) from the silanized titanium surfaces. The spectrophotometer was equipped with a liquid nitrogen ( $T = -196$  °C, STP) cooled HgCdTe<sub>2</sub> (MCT) detector, needed for the reflection absorption infrared (RAIR) accessory (Specac Inc., Smyrna, GA, USA). The incident infrared ray angle was 80°. In this method the object studied was a silane film that absorbed infrared radiation, on a titanium surface. The incident radiation was then reflected on the titanium surface, thus passing the film layer twice.<sup>26,27</sup> Samples were analyzed in an open chamber. The hydrolyzed silane solution was applied to the horizontal surface of a titanium slide and allowed to condensate and react with it. Silane solution hydrolysis reactions were followed up by FTIR with an attenuated total reflectance (ATR) device (Perkin-Elmer Ltd., Beaconsfield, UK), by applying a few drops of fresh silane solution onto the ATR device. The ATR accessory has an inert ZnSe detector that is not known to react with either silanes or the solvents in question according to manufacturer information.

## Results

### Mechanical properties

The highest shear bond strengths for dry samples (20.4 MPa) were obtained by using MPS diluted with



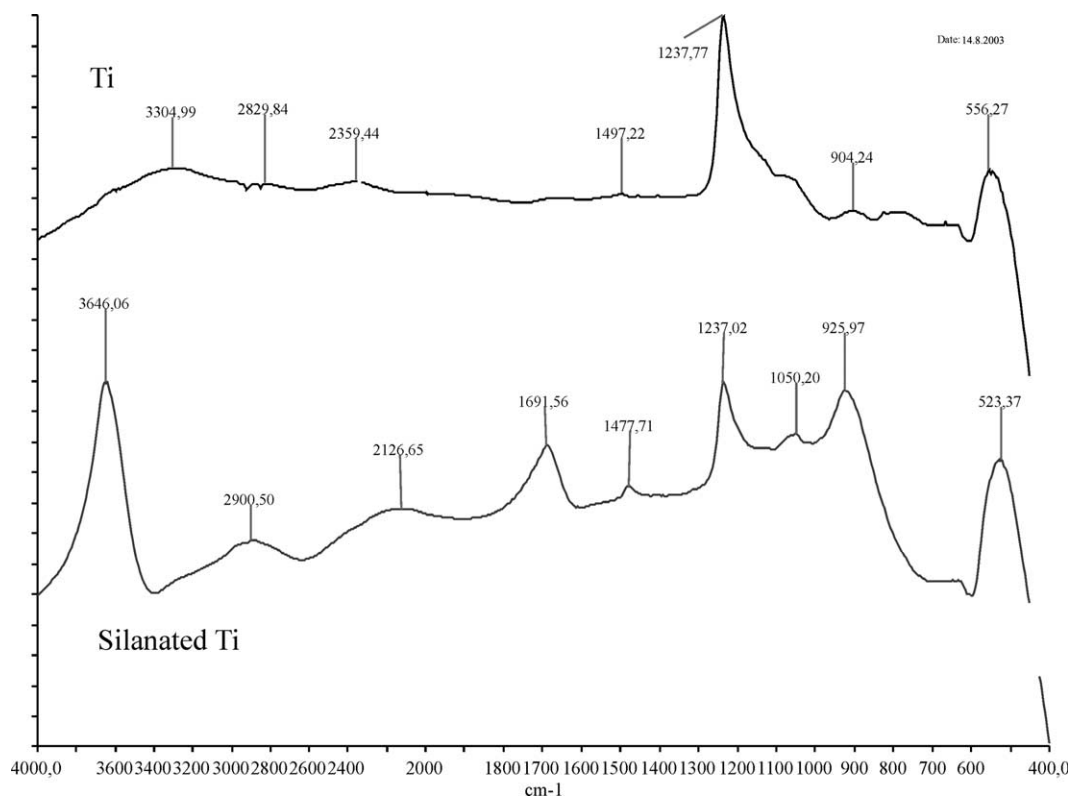
**Figure 4** Shear bond strengths of titanium to Sinfony<sup>®</sup> Veneering composite with various silane, solution and thermal treatments (rt, room temperature; oven, at 110 °C for 1 h. Other abbreviations in this figure: prop, 2-propanol; dmk, acetone; cyan, cyanurate silane; mps,  $\gamma$ -methacryloxypropyltrimethoxysilane; vs, vinyltriisopropoxysilane; cyan, *tris*(3-trimethoxysilylpropyl)-isocyanurate). (Y-axis: Shear bond strength bond strength [F]/MPa).

2-propanol and allowed to condense at RT (Fig. 4). The lowest shear bond strengths were obtained with cyanurate silane and acetone solvent, cured at RT (2.6 MPa). Non-silanized samples yielded 4.8 MPa (SD 2.1 MPa). ANOVA showed that the means differed significantly ( $p < 0.001$ ,  $F = 3.885$ ).

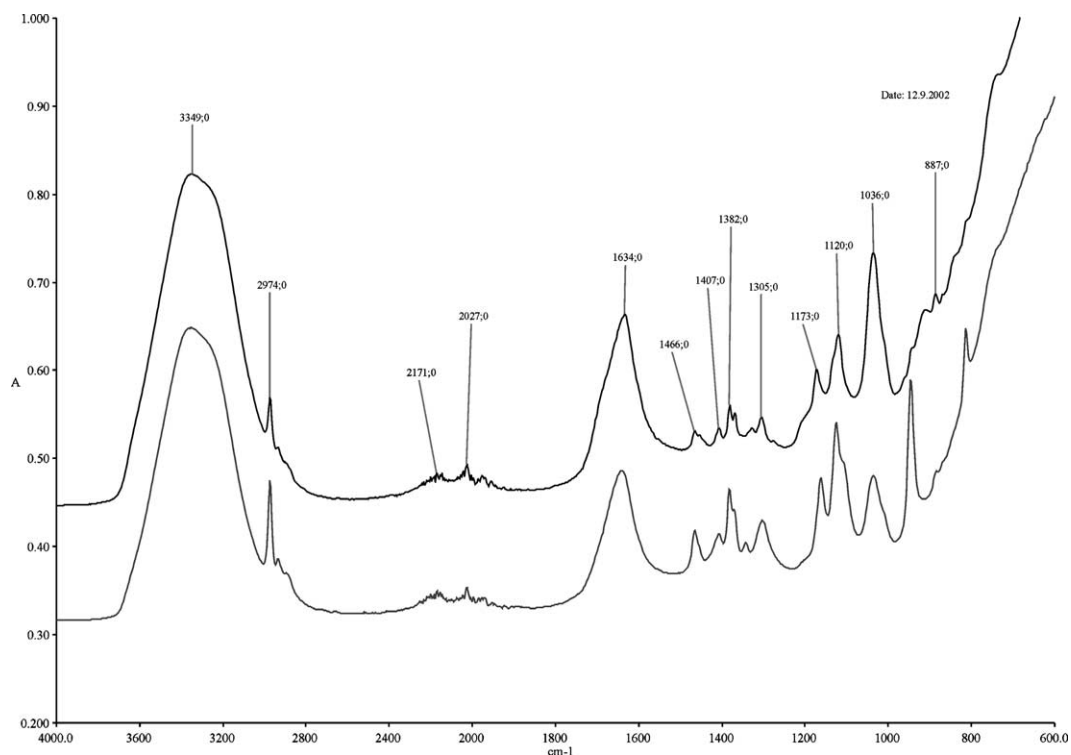
Heat treatment reduced the shear bond strengths in all groups other than with MPS in acetone solvent, and cyanurate silane in both 2-propanol and acetone. Thermocycling also reduced the shear bond and by 3700 cycles the samples were de-bonded from the titanium substrates. Non-silanized composite specimens had already de-bonded from Ti by 3100 cycles.

FTIR results are shown in Figs. 5–8, where absorbance (in arbitrary units) is presented as the function of wave number (cm<sup>-1</sup>). The infrared spectrum analysis showed that hydrolysis of the fresh *tris*(3-trimethoxysilylpropyl)isocyanurate solution took place in under 12 min (Fig. 5): a symmetric C–H stretch of the Si–O–CH<sub>3</sub> group disappeared (ca. 2900–2990 cm<sup>-1</sup>) and Si–OH stretching mode increased (ca. 890 cm<sup>-1</sup>). Appearance of very strong bands at ca. 1055 cm<sup>-1</sup> was due to asymmetric –Si–O–Si– (siloxane network) stretching vibrations. The increase of free hydroxyl groups and water can be seen at ca. 3650 cm<sup>-1</sup> and it also indicates the formation of silanol groups. The hydrogen bonded OH-group band (ca. 3400–3200 cm<sup>-1</sup>) was overlapped by a broad band. While following up the hydrolysis of fresh  $\gamma$ -methacryloxypropyltrimethoxysilane and vinyltriisopropoxysilane blend solution, for 2 h, similar effects could be seen (Fig. 6).

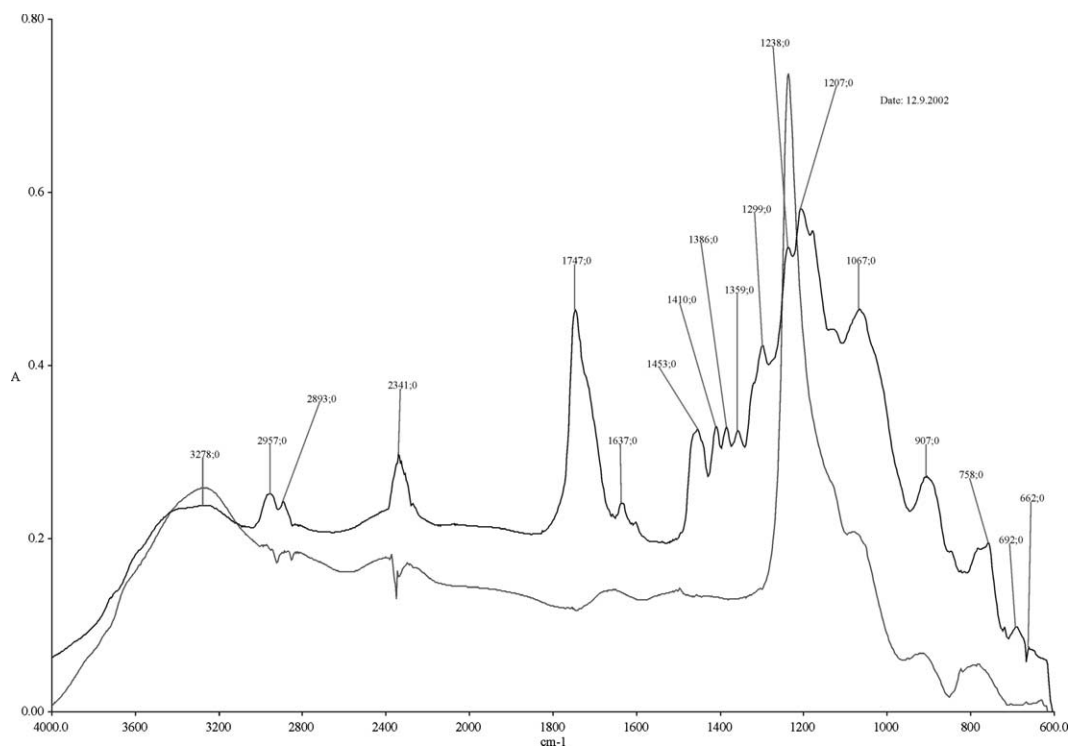




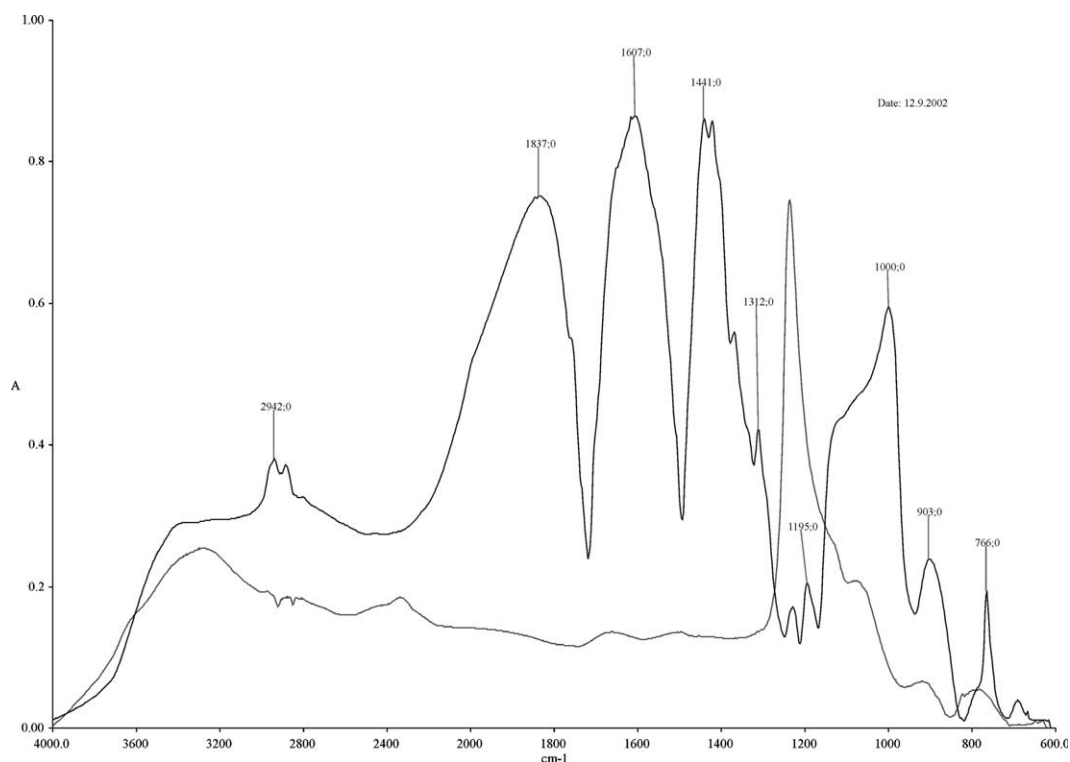
**Figure 5** FTIR spectrum of the hydrolysed 2 wt% *tris*(3-trimethoxysilylpropyl)isocyanurate (in 95% 2-propanol), after 12 min reaction, on titanium surface. X-axis: wave number ( $\text{cm}^{-1}$ ) and Y-axis absorbance A (in arbitrary units).



**Figure 6** FTIR spectra of a fresh 2 wt% blend of  $\gamma$ -methacryloxypropyltrimethoxysilane and vinyltriisopropoxysilane (in 95% 2-propanol), lower spectrum, and after 2 h (upper) at RT. X-axis: wave number ( $\text{cm}^{-1}$ ) and Y-axis absorbance A (in arbitrary units).



**Figure 7** FTIR spectra of a titanium surface without silanization (lower spectrum) and silanized with 2 wt% blend of  $\gamma$ -methacryloxypropyltrimethoxysilane and vinyltriisopropoxysilane (in 95% 2-propanol), cured for 1 h at 110 °C. X-axis: wave number ( $\text{cm}^{-1}$ ) and Y-axis absorbance A (in arbitrary units).



**Figure 8** FTIR spectra of a titanium surface without silanization (lower spectrum) and silanized with 2 wt% *tris*(3-trimethoxysilylpropyl)isocyanurate (in 95% 2-propanol), cured for 1 h at 110 °C.



When silane solutions were applied to a titanium surface and heat treated at 110 °C for 1 h, and titanium surfaces were then analyzed, the following changes were noted: non-silanized Ti-substrates had typically a narrow, very strong band at ca. 1240 cm<sup>-1</sup> that was related to Ti-O- stretching vibrations. They were apparently hidden (overlapped) under a siloxane layer in silanized samples. *Tris*(3-trimethoxysilylpropyl)isocyanurate reacted with the titanium surface. There was no strong band for free hydroxyl groups nor free water at ca. 3690 cm<sup>-1</sup>. The carbonyl stretching band -C=O at ca. 1735 cm<sup>-1</sup> did not change and had no relevance to the adhesion process. At about 1635 cm<sup>-1</sup> there was a characteristic, broad band due to C=C stretching (methacrylate and vinyl groups). In comparison to the hydrolysis spectrum, it did not disappear due to the heat treatment. At ca. 1410-1440 cm<sup>-1</sup> CH<sub>2</sub> groups and vinyl CH<sub>2</sub>=CH- bands were merged together. A vinyl group had also remained. At 1350 cm<sup>-1</sup> the band was due to the methacrylate group. An intense, merged band of siloxane layer, polymerized silane layer could be seen at ca. 1055 cm<sup>-1</sup>. A weak signal of the Si-O-Ti stretching was seen at ca. 920 cm<sup>-1</sup> (Figs. 7 and 8).<sup>8,28,29</sup>

## Discussion

The three silanes that were under study each contains three alkoxy radicals covalently bonded to the silicon atom, being capable of reacting (when first hydrolyzed) with an inorganic substrate, in this case with titanium. The remaining fourth radical of the silane molecule, a polymerizing organofunctional group (methacrylate, vinyl, or isocyanurate) reacts with the monomers of the composite veneering resin.

Hydrolyzed alkoxy groups, i.e. that have reacted with water, turn to silanol groups and as a side product, corresponding alcohol molecules are yielded. The silanol groups bond covalently to the hydroxyl groups (-OH) on titanium dioxide<sup>30</sup> of the titanium surface. Our hypothesis was that silanes of various kinds could react with titanium and thus, in principle, offer improvement in bonding composite resin on the titanium surface when compared with the non-silane treated group.

FTIR spectroscopy is based on infrared absorption and thus on different molecular vibrations, bending, rocking and wagging of the functional groups. Silanes absorb infrared light in the mid-IR region, viz. between 4000 and 600 cm<sup>-1</sup>. It may be used effectively since the inorganic part of the coupling agent yields an extremely strong

absorbance. The spectral subtraction capability of FTIR spectroscopy enables the selective monitoring of the structure of the coupling agent. The FTIR method is convenient, fast and widely applied in silane research.<sup>17,31-33</sup> The spectra are mathematically processed, in order to minimize noise, and to make the spectra comparable.

For the dry samples, the shear bond strengths between titanium samples and Sinfony<sup>®</sup> veneering composite are shown in Fig. 4. Non-silanized samples yielded 4.8 MPa (SD 2.1 MPa). Most values exceeded the relatively limiting low bond value, which is 5 MPa according to ISO standard 10477.<sup>34</sup> The shear bond strength for thermocycled samples could not be measured since the samples were debonded by 3700 cycles. This demonstrates that bonding with titanium by using MPS + vinylsilane (VS) or cyanurate silanes was not effective. However, it should be taken into consideration that the thermal expansion coefficient of titanium ( $8.5 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ )<sup>35</sup> varies greatly from that of the veneering composite ( $54 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ ).<sup>36</sup> The temperature change of the thermocycling could destroy even durable attachment of materials with different thermal coefficients. One possible solution for eliminating this problem could be the use of a resilient adhering interface between the materials. On the other hand, MPS offered relatively high bond strength for the composite resin. This agrees with the work by Ekstrand et al.<sup>17</sup> The heat treatment seemed to yield strong absorption bands, speaking for strong siloxane (-Si-O-Ti-) network bonding on the titanium surface.

*Tris*(3-trimethoxysilylpropyl)isocyanurate does not clearly have an end ready to polymerize with the composite resin (cf. Fig. 2), so the certain tendency to act as a size may be explained by an interpenetrating polymer network (IPN) model in which the organic end of the silane molecule forms an interpenetrating film, interface, with the composite. This layer can be described as a molecular level nanomechanical retention.<sup>37,38</sup> In optimal conditions, this IPN layer could behave as a resilient adhesive interface layer. Generally, the silane film thickness is not dependent on contact time, but on the silane concentration.<sup>38</sup>

The flashpoint for pure *Tris*(3-trimethoxysilylpropyl)isocyanurate is 102 °C. The boiling points for vinyltriisopropoxysilane is 179-181 °C, and for MPS 78-81 °C.<sup>39</sup> In Fig. 4 it can be seen that 'cyan' treatment at 110 °C did not give the lowest results. On the other hand, RT gave the best results for MPS and MPS + vinylsilane. The curing temperature beyond the boiling point for a silane might be an important factor, however, this should be studied closer. The acetone-water and 2-propanol

comparison needs further studies, especially for these tests, since acetone-water and MPS + vinylsilane gave a slightly milky solution, indicating most probably that the silane was oxidized to colloidal silica. Since MPS is known to perform in acetone-water solvent in dental silanes, the silica may derive from the vinylsilane.<sup>40</sup> These interactions have been studied with some silanes and a silica surface.<sup>41</sup> More solvent effect studies could be undertaken in future.

In this study,  $\gamma$ -methacryloxypropylsilane behaved less effectively than might have been thought. However, the weakness in adhesion may depend on the fact that the siloxane layer was deteriorated by moisture. Also, the silane layer was applied to the Ti by brushing, exactly as under clinical conditions.<sup>25</sup> However, the siloxane film is not necessarily equally uniform throughout the surface. More tests (for silane concentration, contact angle measurements, 2-propanol concentration, the hydrolysis time) can be encouraged. Silanes appear to have a role (though also disputed) in the adhesion processes while bonding composite resin to titanium and other substrates relevant in dentistry.

## Conclusions

The experiments and results, with the limitations of this study, led the authors to the following conclusions:

1. Bond strength of composite to titanium in dry conditions showed significant differences. 2-propanol may be used as a solvent for MPS, while 90% acetone as a solvent for silanes exhibited inferior results.
2. Bonding of composite to titanium metal, by coupling with a *tris*(3-trimethoxysilylpropyl)isocyanurate solution, either in aqueous 2-propanol or 90% acetone solution could not form a thermally stable bond to the composite. Heat treatment may enhance the bonding by forming an interpenetrating network at the interface. However, for the MPS in acetone and MPS + VS in acetone solutions, heat treatment did not show any remarkable difference.
3. FTIR analysis showed that metallo-siloxane bonding to a titanium surface (-Si-O-Ti-), and pure siloxane bond formation (-Si-O-Si-) have both been successful, viz. strong spectral bands can be seen, and bands indicating that both hydrolysis and condensation reactions of silanes has occurred. The heat treatment seemed to yield strong absorption bands, speaking apparently for a strong siloxane network formation on the titanium surface.
4. MPS type silane seems to have a significant role as a coupling agent for bonding composite resin to Ti substrate when compared to the non-silanized group.

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